

AD-A104 086

MARYLAND UNIV COLLEGE PARK DEPT OF CHEMISTRY  
DIELECTRIC CONSTANT OF UNDERCOOLED WATER.(U)

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SEP 81 B K DAS, G F KRAUS, J T SIEWICK

N00014-79-C-0008

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1. REPORT NUMBER 2		2. GOVT ACCESSION NO. AD-A104086		3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Dielectric Constant of Undercooled Water.		5. TYPE OF REPORT & PERIOD COVERED Technical Report.		6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) B.K./Das, G.F./Kraus, J.T./Siewick and S.C./Greer		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0008		9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Maryland College Park, MD 20742	
10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		11. REPORT DATE September, 1981		12. NUMBER OF PAGES 21	
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		14. SECURITY CLASS. (of this report) Unclassified		15. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.					
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)					
18. SUPPLEMENTARY NOTES To appear in "Proceeding of the Eighth Symposium on Thermophysical Properties", published by the American Society of Mechanical Engineers.					
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Dielectric constant, conductivity, supercooled water, undercooled water.					
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Recent work has shown that liquid water has anomalous thermodynamic properties in its metastable undercooled state, below 0°C. We have investigated the static dielectric constant and conductivity of undercooled water by measuring the capacitance (within 0.05%) and conductance (within 0.2%) of water-filled glass capillary capacitance cells between +20°C and -17°C. We find that the capacitance and conductance data over the entire temperature range can be represented by analytic functions. Our measurements show no evidence of anomalous behavior in the dielectric constant or conductivity of undercooled water.					

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Task No. NR 051-701

TECHNICAL REPORT NO. 2

Dielectric Constant of Undercooled Water

by

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and S.C. Greer

Prepared for Publication  
in the

Proceedings of the Eighth Symposium of Thermophysical  
Properties (American Society of Mechanical Engineers)

University of Maryland  
Department of Chemistry  
College Park, MD 20742

September 3, 1981

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Dielectric Constant of Undercooled Water

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Eighth Symposium on Thermophysical Properties  
National Bureau of Standards, June 15-18, 1981

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# ABSTRACT

Recent work has shown that liquid water has anomalous thermodynamic properties in its metastable undercooled state, below  $0^{\circ}\text{C}$ . We have investigated the static dielectric constant and conductivity of undercooled water by measuring the capacitance (within 0.05%) and conductance (within 0.2%) of water-filled glass capillary capacitance cells between  $+20^{\circ}\text{C}$  and  $-17^{\circ}\text{C}$ . We find that the capacitance and conductance data over the entire temperature range can be represented by analytic functions. Our measurements show no evidence of anomalous behavior in the dielectric constant or conductivity of undercooled water.

## I. Introduction

The study of undercooled (or supercooled) water--water in a metastable liquid state at temperatures below the freezing point--has received considerable attention in recent years.<sup>[1]</sup> Many of the physical properties of undercooled water, such as the isobaric heat capacity, the isothermal compressibility, and the viscosity, change dramatically with the degree of undercooling. The behavior of these properties suggests that there may be a "transition temperature" at about  $-45^{\circ}\text{C}$ . While several theories have been advanced to explain the anomalous behavior of undercooled water<sup>[2-6]</sup>, these models are at best qualitative, relating in one way or another to the effects of hydrogen bonds developing in the water. At present, we have no quantitative theory to explain the interesting phenomena observed in undercooled water.

Much of the work on supercooled water has been done on emulsions in hydrocarbon solvents because such emulsions allow supercooling of as much as  $35^{\circ}\text{C}$ .<sup>[1]</sup> Bulk water in volumes less than  $1\text{ cm}^3$ , carefully cleaned and held in very clean cells, can be cooled as much as  $20^{\circ}\text{C}$ .<sup>[1]</sup>

In an effort to add to the experimental information on undercooled water, we have undertaken measurements of the static dielectric constant,  $\epsilon$ , of undercooled bulk water at 1 atm. The static dielectric constant of undercooled water was first measured by Rusche and Good<sup>[7,8]</sup> in the range  $-5^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$  using bulk samples of about

20 cm<sup>3</sup>. The static dielectric constant of emulsified water was measured to -35°C by Hasted and Shahidi<sup>[9]</sup> and by Hodge and Angell<sup>[10]</sup> who deduced  $\epsilon$  for the water from measurements of the dielectric constant and dielectric loss of the emulsions as functions of frequency, using the theory of inhomogeneous dielectric media.<sup>[11,12]</sup> The emulsion method involves several approximations<sup>[9,10]</sup> which limit its accuracy to 1-2%; finite size effects could also be a source of systematic error.<sup>[3]</sup> We note that none of these data showed unambiguously anomalous behavior of  $\epsilon$  in the undercooled region.

Our aim has been to measure the static dielectric constant of undercooled water with greater accuracy and precision by using bulk water in very small coaxial capillary dielectric cells. We have achieved supercooling of as much as 17°C in these cells. The capacitance of the filled cells, precise to 0.05% or better, shows no indication of an anomaly in the dielectric constant as the water is undercooled, nor is there any alteration in behavior at 0°C. Since the empty cell capacitance is also analytic, we conclude that the dielectric constant of undercooled water must be a smooth continuation of that of normal water. The design of our present cells has precluded an accurate conversion of the capacitance information into absolute dielectric constant information.

## II. Experimental Method

A. Capacitance cells: The capillary coaxial capacitance cells follow the design shown in Fig. 1. These cells allow

the use of very small amounts of water to maximize the degree of supercooling, while the coaxial geometry provides good mechanical stability.

The cell is prepared from quartz capillary tubes which are first etched for 5 min. with 5% aqueous HF, then thoroughly rinsed with distilled water. Our experience has been that the HF etching increases the undercooling by about 5°C as compared to unetched tubes. We also tried coating the cells with hydrophobic agents, but found no increased supercooling with such coatings and discontinued using them.

The tubes are then nearly filled at 1 atm with very pure water.<sup>[13]</sup> The water, distilled in a quartz still at 1 atm, is degassed by several freeze-pump-thaw cycles, then injected into the cell by a syringe through a 0.22  $\mu\text{m}$  filter.

The platinum wire which forms one electrode of the capacitance cell is centered in the cell using a jig to hold all components rigid. The wire is then secured with low vapor pressure epoxy.<sup>[14]</sup> Since surface tension holds the water in its vertical position, the epoxy is not in contact with the water. The other electrode is formed by painting the outside of the tube with conducting silver paint.<sup>[15]</sup> The volume surrounded by the paint is completely filled with water. We have made cells either 2.5 cm or 5 cm in length, with corresponding cell volumes of 0.1  $\text{cm}^3$  or 0.2  $\text{cm}^3$ . We note that the outer electrode



encloses the quartz cell wall as well as the water; we discuss this complication below.

B. Temperature control and measurement: The thermostat is a multistage vacuum one of conventional design<sup>[16]</sup>, consisting of an outer vacuum can, an inner can or radiation shield, and the experimental stage. The two cans are evacuated to about  $10^{-3}$  mm Hg. The outer can is made of aluminum and is wrapped with aluminum tubing through which a commercial circulator-cooler pumps a circulating fluid with its temperature controlled to 20 mK between  $-50^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ . The radiation shield is made of copper and is wrapped with a heater wire. A thermistor<sup>[17]</sup> on the radiation shield is used to control the temperature of the radiation shield to about 1 mK by means of a digital temperature control system.<sup>[16]</sup>

A platinum resistance thermometer (PRT) and as many as 4 capillary capacitance cells are mounted on the copper experimental stage. The resistances of the thermistor and of the PRT are measured by placing each in series with a standard resistor and a mercury battery and measuring the voltage drops across the thermometers as compared to those across the standard resistors.<sup>[16]</sup> The cell temperature is given on the International Practical Temperature Scale of 1968 by the PRT with a resolution of 3 mK.

C. Capacitance measurements: Coaxial cables lead from the cells, through coaxial feedthroughs on the thermostat, to a General Radio 1615A capacitance bridge operated at 40 kHz. The capacitance measurements are three-terminal. The cells

do not have guard rings and are thus subject to edge effects which could be as much as 0.2%. The resolution of the capacitance bridge is  $10^{-4}$  pf. The bridge also measures the series conductance D (the dissipation factor) of the cells with a resolution of 0.2%. D is related to the parallel conductance G by  $G = 2\pi fCD$ , where f is the frequency in Hz, C is the capacitance in farads, and G is in  $\Omega^{-1}$ .

Measurements are made on the filled cells from room temperature to the freezing temperature of the undercooled water, after which the cells are cracked to allow the water to be pumped out by the thermostat vacuum system. Care is taken to try to maintain the cell geometries in the empty cells. Measurements are then made of the capacitance of the empty cells over the same temperature range; these data are not always as reproducible as those for the filled cells due to lack of mechanical rigidity in the broken cells.

For the 2.5 cm long cells, the filled cells have had capacitances of about 33 pf and the empty cells of 1-2 pf. D is about  $10^{-3}$  for a full 2.5 cm cell and  $10^{-4}$  for the empty cell. The conductivity of the water in the cells was estimated from the conductance of the cells to be about  $2 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ .

### III. Results and Analysis

Fig. 2 shows the total capacitance of the filled cell,  $C_F^T$ , as a function of temperature, T, for several runs on a typical capacitance cell. ( $C_F^T$  decreases with cooling, even though  $\epsilon$  increases<sup>[8-10]</sup>, because the capacitance of the empty cell decreases with temperature more than the

$\epsilon$  of the water increases.) In a given cooling sequence of a cell, the precision of the  $C_F^T$  measurements, as expected from the propagation of errors from the capacitance and temperature measurements, is about 0.02%. The reproducibility on subsequent cooling sequences is 0.03-0.05%; we assume the increased scatter is due to mechanical hysteresis.

We find that a quadratic polynomial function can be fitted to the  $C_F^T(T)$  data to within the uncertainty of the measurements. We have chosen not to analyze the ratio of  $C_F^T(T)$  to the total capacitance of the empty cell,  $C_E^T(T)$ , because the reproducibility of  $C_E^T(T)$  is rarely as good as that of  $C_F^T(T)$ .

The conversion of  $C_F^T(T)$  to  $\epsilon(T)$  of water is complicated by the fact that both the water and the quartz cell wall are between the capacitor plates. The total capacitance of a filled cell,  $C_F^T$ , consists of the series combination of the capacitance of the quartz wall,  $C_Q$ , and that of the water,  $C_W$ :

$$C_F^T = C_W C_Q / (C_W + C_Q). \quad (1)$$

Likewise, the total capacitance of an empty cell,  $C_E^T$ , is

$$C_E^T = C_V C_Q / (C_V + C_Q), \quad (2)$$

where  $C_V$  is the capacitance of the vacuum.

If we define the ratios:

$$R = C_F^T / C_E^T \quad (3)$$

$$\alpha = C_V / C_Q \quad (4)$$

then we can show that the dielectric constant  $\epsilon$  of the water is related to  $R$  and  $\alpha$  by

$$\epsilon^{-1} = [1 + \alpha(1-R)]/R \quad (5)$$

Thus, the determination of an absolute value of  $\epsilon$  from our data at any given temperature requires not only the experimentally measured value of  $R$ , but also the quantity  $\alpha$ , which we cannot measure.

We have attempted to determine  $\alpha$  by using the  $\epsilon$  data of Malmberg and Maryott<sup>[18]</sup> above  $0^\circ\text{C}$ , together with our  $R$  data and equation 5, to calculate  $\alpha$  above  $0^\circ\text{C}$ , from which we can extrapolate  $\alpha$  to below  $0^\circ\text{C}$  in order to calculate  $\epsilon$  below  $0^\circ\text{C}$ . We have been disappointed to find that these extrapolations are usually so uncertain (several percent) as to be uninformative. Within their rather large uncertainties, the  $\epsilon(T)$  plots so obtained are consistent with the emulsion results.<sup>[9,10]</sup>

The total series conductance of the filled cell as a function of temperature,  $D_F^T(T)$ , is shown in Fig. 3. The cell is the very same one on which the data in Fig. 2 were taken. The scatter of these measurements is about 0.2% within a run and 0.4% among runs.  $D_F^T(T)$  increases as  $T$  decreases, but the behavior is not nonanalytical.  $D_F^T(T)$  can be represented within the experimental uncertainty by an analytical function (for example, a cubic polynomial). The conversion of  $D_F^T(T)$  to absolute conductivity values for water involves considerations similar to

those discussed above for the conversion of  $C_F^T(T)$  to  $\epsilon(T)$  of water and was not attempted. However, since the conductance of the empty cell decreases as  $T$  decreases, our data seem to indicate that the conductivity of the water increases as  $T$  decreases, which is inconsistent with the data of Hodge and Angell [10]. We have not resolved this discrepancy.

#### IV. Conclusions and Discussion

The issues which led us to these experiments are:

- 1) Is there anomalous behavior in  $\epsilon(T)$ , the dielectric constant as a function of temperature, in undercooled water at 1 atm? [10]
- 2) Is there a change in the slope of  $\epsilon(T)$  of liquid water at or near  $0^\circ\text{C}$ , the normal freezing at 1 atm? [9,19]
- 3) Is there an anomaly in the conductivity as a function of temperature,  $\sigma(T)$ , in undercooled water at 1 atm? [10]
- 4) Is there a change in slope of  $\sigma(T)$  at  $0^\circ\text{C}$  and 1 atm?
- 5) Do  $\epsilon$  and  $\sigma$  measurements taken on bulk water agree with measurements made on emulsified water? [9,10]

Let us consider the first two issues. Our measurements on the capacitance of water-filled cells indicate that the behavior of  $\epsilon$  of liquid water at  $0^\circ\text{C}$  is an analytic continuation of the behavior above  $0^\circ\text{C}$ , within our precision of 0.05%. We do not expect the 0.2% edge effects to affect this conclusion.

Our conclusion for the third and fourth issues is similar. Within our uncertainty of 0.2%, we find that the conductivity of liquid water at and below  $0^{\circ}\text{C}$  is an analytic continuation of the conductivity above  $0^{\circ}\text{C}$ .

We are unable to make a good comparison with the emulsion results[9,10], since we cannot convert to an absolute  $\epsilon$  scale. We observe no discrepancy with those results on  $\epsilon$  within the combined experimental uncertainties. We seem to see an increase in  $\sigma$  on cooling, whereas Hodge and Angell[10] observe a decrease.

We have under development new capillary capacitance cells which have the outer electrode on the inside of the glass wall. We hope to obtain absolute  $\epsilon$  data and to better understand the behavior of the conductivity of supercooled water by using these cells.

#### V. Acknowledgements

We are pleased to acknowledge the support of the Office of Naval Research. We thank C.T. Van Degrift for the loan of the capacitance bridge.

This research is taken from a dissertation to be submitted to the Graduate School, University of Maryland, by George F. Kraus in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

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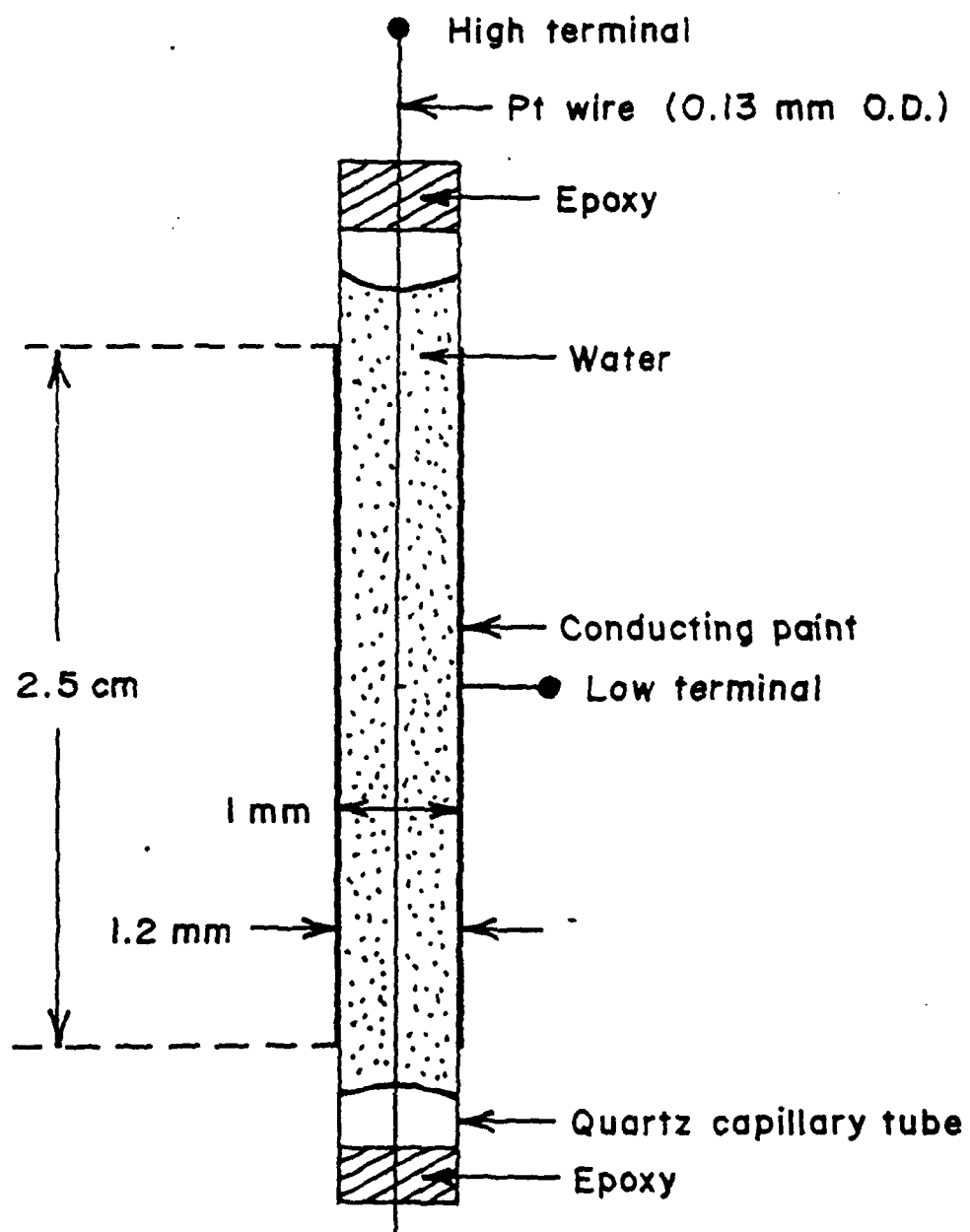
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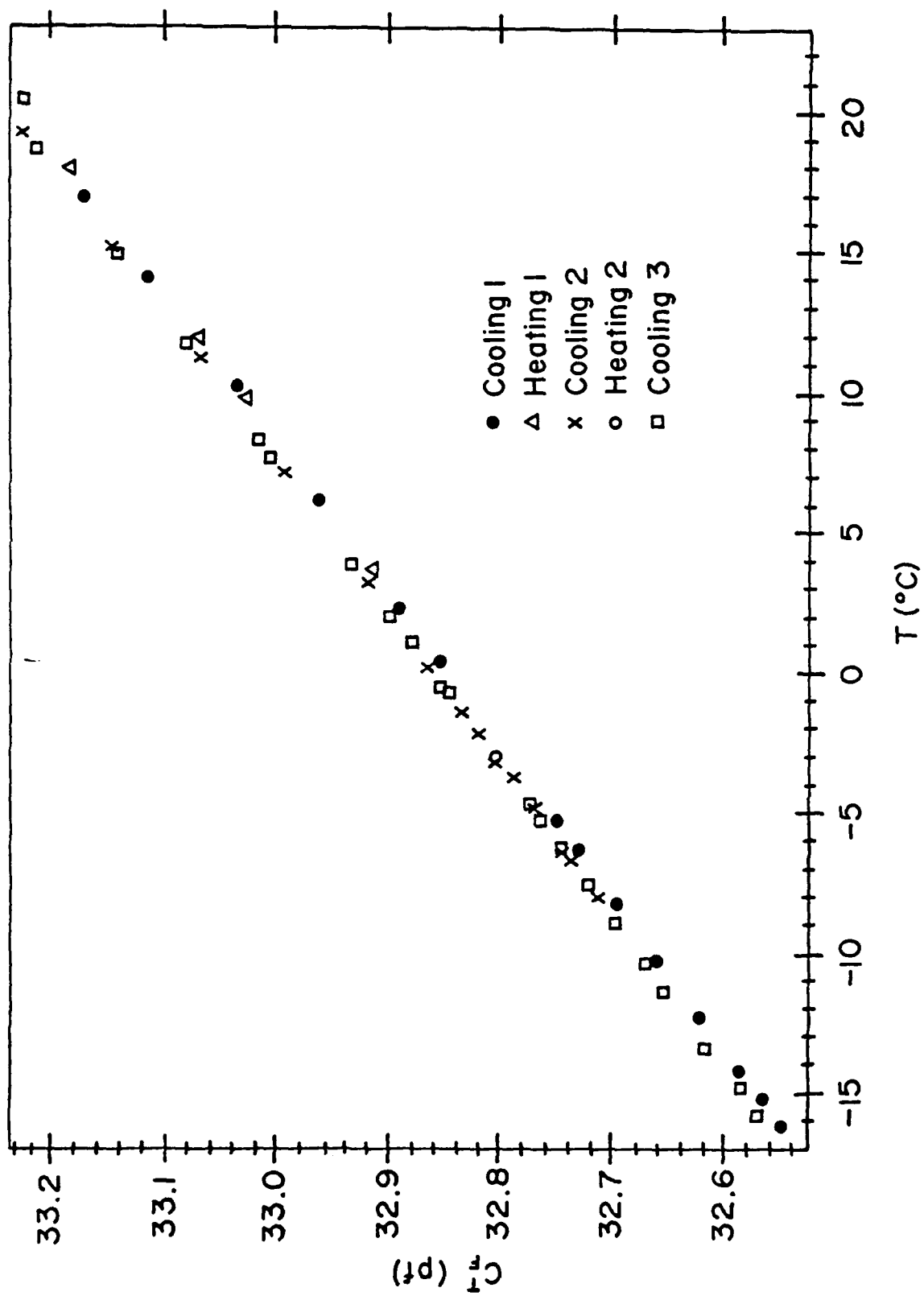
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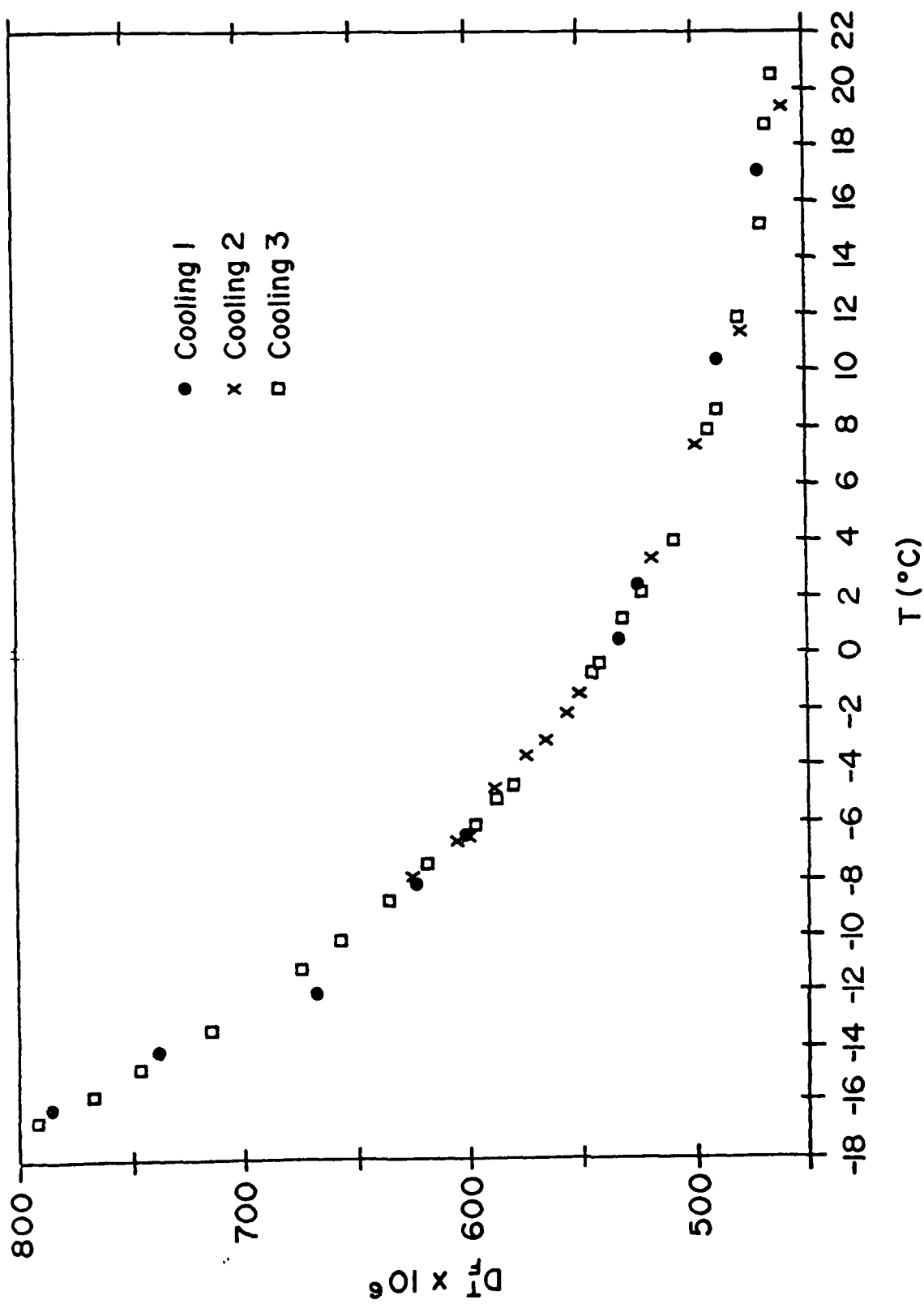


## FIGURE CAPTIONS

- Figure 1: Coaxial capillary capacitance cell for investigation of dielectric constant of undercooled water.<sup>3</sup> The volume of the water in this cell is 0.1 cm<sup>3</sup>.
- Figure 2: Measurements of the capacitance of a typical capillary cell (see Fig. 1) filled with water as a function of temperature. Different symbols denote different cooling sequences.
- Figure 3: Measurements of the series conductance of the filled capillary cell used in Fig. 2 as a function of temperature. Different symbols indicate different cooling sequences.







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